

EXTRACTION OF LIMONITE NICKEL ORE OF TANJUNG BULI, HALMAHERA BY COAL ROASTING AND ACID LEACHING

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ABSTRACT

This research aims to increase limonite nickel ore concentration by coal roasting and acid leaching process. The extraction of nickel by the pyro-hydrometallurgy method with coal reduction roasting and acid leaching was performed after the washing and drying process. Reduction roasting used 20 wt.% of coal with a temperature 500–800 °C and roasting time 20-60 minutes. Leaching process used HCl 1 :1 solution. In the washing and drying processes, the nickel concentration was increased by 13.72%. The roasting process at 500 –600 °C required roasting time for 40-60 minutes while at roasting temperature 700 °C, the required time for 20 minutes, faster than the lower temperature. In the leaching process, samples were reduced at higher temperatures resulting in a higher nickel extraction. Roasting reduction at 800 °C for 20 minutes has increased the nickel concentration by 29.33%. Leaching samples roasted at 800 °C for 60 minutes provide the best nickel extraction result with percentage ratio of nickel and iron as 14.42.

KEYWORDS: *Limonite Nickel, Coal Roasting, Acid leaching & Extraction*

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INTRODUCTION

Nickel metals in nature are found in various forms of minerals, but the main ones are sulfide and oxide. In Indonesia, nickel limonite has spread to several locations in Kalimantan, Sulawesi, Maluku Islands and Papua[1, 2]. The process of nickel ore can generally be categorized as pyrometallurgy, pyro-hydrometallurgy and hydrometallurgy pathways[3, 4]. For ore processing of low nickel-based, several processes can be used with the advantages and disadvantages of the process so that the selection process is the result of the optimization of various conditions that exist. This research aims to find out the main elements and phases of limonite nickel of Tanjung Buli, increasing the concentration of nickel with the washing process, drying and reducing roasting with coal and determining the optimum conditions of dissolving and percentage of extraction of nickel on acid leaching.

MATERIALS AND METHODS

Materials

Raw materials. The samples used came from Tanjung Buli, Halmahera with sample code IC BIII/B5 – 14/25, KED: 1 M, 10 KG belongs to PT. Aneka Tambang, Tbk.

Supporting materials. HCl p.a. 37%, aquadest, coal from PT. Adaro East Kalimantan and buffer solution pH 4 and pH 7.

Equipment

Laboratory equipment and supporting equipment such as electric OvenMettler, Furnace 30400, Magnetic stirrer, Atomic Absorption spectrophotometer (AAS) Spectra 20 Plus variant, Sizing, Sartorius CP-622 scales, BP 221 S

Sartorius weigher and Automatic head-over 798 MPT, PT. Aneka Tambang, Tbk., *X-Ray fluorescence* (XRF) Jeol JSX-3211 of the Department of Physics, the University of Indonesia, as well as *X-Ray Diffractometer* (XRD) type PW 1710 BASED and EDX of the Department of Metallurgical and Material Engineering, University of Indonesia.

Procedure

Samples were characterized by using XRF and XRD. A sample of dark brown soil was stirred to be homogeneous. The samples were overflowing by water with a constant rate of 72 mL/s. Overflow is conducted in three batches with different diameters. A sample was precipitated for 3 hours. After precipitation was performed, there are impurities such as foam and roots that float on the surface. Impurities are disposed of by decantation. Decantation is conducted until the water slightly and maintained so that the sample was not wasted. The next process was drying. The drying technique is carried out at a temperature of 105°C for 48 hours with an electric oven. Then the grinding and sizing techniques were done in order for the dried samples and made coal to be homogeneous. The size of the material used was 100 mesh. Then the samples were characterized by XRF while the coal was characterized by EDX.

The reduction technique was carried out by mixing of 80 wt.% limonite (16 g) and 20. wt% of coal (4 g) in a crucible and inserted into the furnace. The variation of temperature was 500 °C, 600 °C, 700 °C and 800 °C and time variation for 20 minutes, 40 minutes and 60 minutes. Samples of this reduction roasting result were characterized using XRF and XRD. The final process was leaching and filtration. The leaching technique was carried out with the 1:1 HCl solvent by a volume ratio of 1:1 between HCl p.a. with the aquadest. The leaching performed at a temperature of 60 °C for 15 minutes. After the leaching process was completed, then the next process is filtration. The resulting filtrate was characterized by Atomic Absorption Spectrometer (AAS).

RESULTS AND DISCUSSIONS

Based on the results of characterization with XRF, the initial sample of limonite contains eight elements, i.e. Aluminium (Al), Silicon (Si), Sulfur (S), Titanium (Ti), Vanadium (V), Chrom (Cr), Iron (Fe) and nickel (Ni) with a percentage that can be seen in Table 1.

Table 1: Weight Percentage of the Element characterized by XRF

Elements	Atomic Number	Weight Percentage of the Element (wt%)
Al	13	11.0881
Si	14	3.9249
S	16	0.3787
It	22	0.8477
V	23	0.0323
Cr	24	1.9787
Fe	26	80.6290
Ni	28	1.1206

In addition to XRF, the initial sample of limonite is also characterized by XRD and provides diffraction peaks as shown in Figure 1.

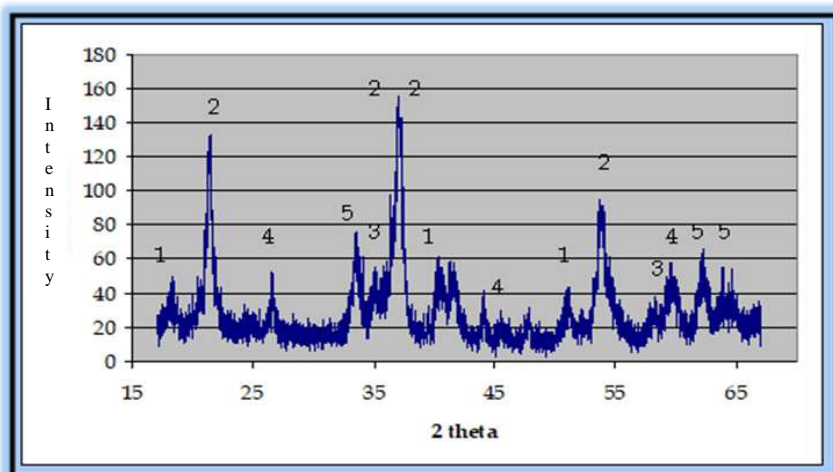


Figure 1: The Peaks of the Initial Sample Diffraction of Limonite.

The phase peaks explanation can be seen in Table 2. The above phase determination was obtained after D-Spacing of limonite (observation) compared with D-spacing reference/calculated by looking at the three the strongest D-spacing value (Table 3). The following is the output distance between fields (D-spacing α_1) which proves the existence of phases as predicted using PCPDFWIN Software.

Table 2: Peak Phase Accompanied by PDF Number, Crystal System and Space Group

No.	Phase	PDF Number	Crystal System and Space Group
1	Gibbsite $\text{Al}(\text{OH})_3$	76-1782	Monoclinic P_{21}/c (14)
2	Goethite $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$	08-0097	Orthorhombic, PBNM (62)
3	Chromite $\text{Cr}_2\text{O}_3 \cdot \text{NiO}$	77-0008	Cubic $Fd\bar{3}m$ (227)
4	Quartz SiO_2	83-0539	Hexagonal P_{3121} (152)
5	Hematite, Fe_2O_3	01-1053	Rhombohedral $R\bar{3}c$ (167)

Table 3: Distance Between Fields (D-Spacing) Early Sample Limonite

Sl. No.	D-Spacing		Phase	Relative Intensity (%)	hkl
	Calculated	Observation			
1	4.8340	4.8439	Gibbsite	45.20	002
2	4.2100	4.1297	Goethite	100.00	110
3	3.3492	3.3415	Quartz	24.10	101
4	2.6900	2.6685	Hematite	31.40	104
5	2.5022	2.5598	Chromite	17.80	311
6	2.4800	2.4724	Goethite	75.80	040
7	2.4400	2.4172	Goethite	71.40	111
8	2.2416	2.2271	Gibbsite	17.80	022
9	2.1559	2.1629	Gibbsite	15.00	312
10	2.0747	2.0551	Chromite	12.50	400
11	1.9829	1.9927	Quartz	5.40	021
12	1.7989	1.7834	Gibbsite	7.10	322
13	1.6890	1.7022	Goethite	25.90	240
14	1.5971	1.5825	Chromite	6.20	511
15	1.5439	1.5504	Quartz	11.90	211
16	1.4900	1.4961	Hematite	11.90	214
17	1.4500	1.4542	Hematite	9.10	300

The washing and drying process at a temperature of 105°C resulted in a sample depreciation of 32.83%. This large depreciation is caused by removal of impurities. When the decantation is performed and the release of H_2O during the

drying process, as it is, generally nickel limonite contains high humidity of up to 45% [1] which is evident in the presence of the gibbsite and goethite phases containing H_2O . In the washing process by overflow, particles were distributed so that nickel concentration occurred in the three batches with the percentage showed in Table 4.

Table 4: Increasing of Nickel Concentration after Washing and Drying Process

Batch	Nickel Concentration (%)
First	6.22
Second	9.82
Third	13.72

The characterization of coal using EDX with three measurements provides information that the coal of PT. Adaro East Kalimantan contains elements of Carbon (C), Oxygen (O), Silicon (Si) and Sulfur (S) with the average content that can be seen in Table 5.

Table 5: Weight Percentage of the Elements on Coal

Elements	Atomic Number	Weight Percentage of the Element (wt.%)
C	6	63.16
O	8	31.36
Si	14	0.83
S	16	4.66

In general, coal contains SiO_2 and sulfur. SiO_2 is seen in the presence of white grains on coal. This coal is used as a reduction agent where the carbon oxidation produce gas CO_2 will continue with the formation of gas CO with excess coal. The formation of gas CO is known as Carbon Solution Loss because there is carbon dissolving in gas CO_2 . Gas is this CO reduction agent that will be used to reduce metal oxide.

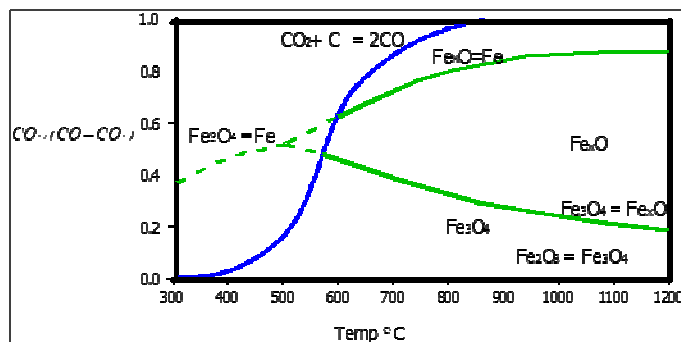


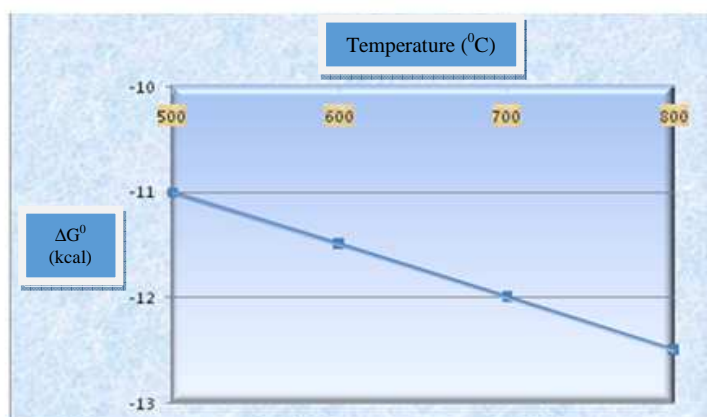
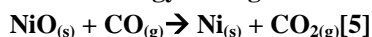
Figure 2: Boudouard Equilibrium[5]

Based on the Boudouard equilibrium found in figure 2 above, the increasing roasting temperature will increase the production of gas Reductors CO . The gas production increasing CO can be seen in Table 6.

Table 6: Percentage of Gas Formation CO₂ and CO with a Total Pressure of 1 atm

Temperature (°C)	% CO ₂	% CO
450	97	3
500	93	7
600	74	26
670	50	50
700	39	61
800	12	88
900	3	97
1000	1	99

Gas CO is used to reduce the nickel oxide and iron oxide into nickel and iron metals. A reduction of NiO becomes Ni in the exothermic at 500–800°C meaning that the NiO reduction is easier to occur in the temperature range of 500–800°C as shown in Figure 3.

**Figure 3: Gibbs Free Energy Changes of Reduction Process**

Based on the Boudouard equilibrium and changes in the free energy Gibbs's NiO reduction, we can estimate the reduction in the production of limonite with coal. On the roasting temperature of 500 °C (Table 7) occurred the reduction hematite (Fe₂O₃) into magnetite (Fe₃O₄). The formed magnetite could not be reduced to Fe due to the formation of the new FeO stable at a temperature of 560 °C [6].

Table 7: Phase Reduction in Limonite and Coal Roasting

Temperature (°C)	Phase of Reduction Result
500	Fe ₃ O ₄ and Ni
600	Fe ₃ O ₄ , FeO, Fe and Ni
700	Fe ₃ O ₄ , FeO, Fe and Ni
800	Fe ₃ O ₄ , FeO, Fe and Ni

Other oxides such as Al₂O₃, SiO₂ and Cr₂O₃ cannot be reduced by CO due to need a greater pressure ratio of CO/CO₂ compared to nickel oxide reduction. The characterization of limonite roasting results with XRD resulting in a phase peak as seen in Figure 4. The phase peaks explanation can be seen in Table 8.

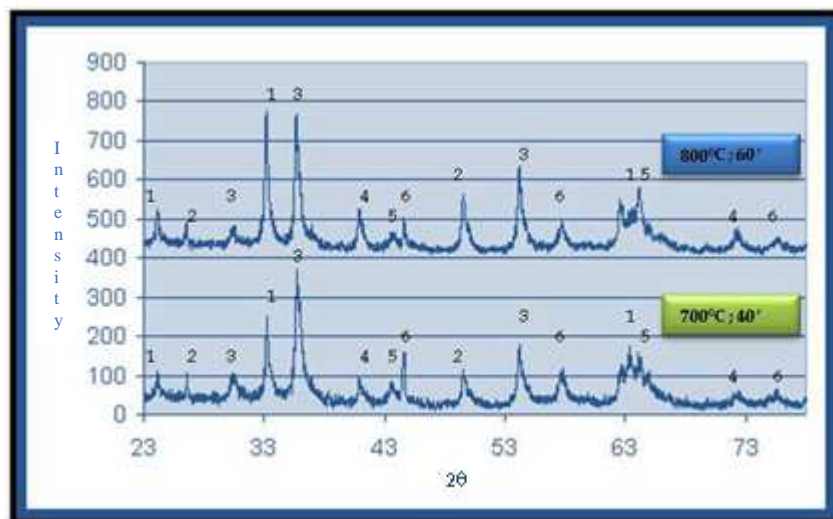


Figure 4: The Peaks of the Roasting Limonite.

Table 8: Phase Peaks Accompanied by PDF Number, Crystal System and Space Group

No.	Phase	PDF Number	Crystal System and Space Group
1	Hematit, Fe_2O_3	01-1053	Rhombohedral, P-3c (167)
2	Quartz, SiO_2	83-0539	Hexagonal, P_{3121} (152)
3	Magnetite, Fe_3O_4	75-0449	Cubic, Fd3m (227)
4	Wustite, FeO	74-1886	Cubic, Fm3m (225)
5	Iron, Fe	01-1253	Cubic, Im3m (229)
6	Corundum, Al_2O_3	02-1373	Rhombohedral, P-3c (167)

Chromite does not appear in XRD characterization due to the roasting process. Chromite has been degradable into Cr_2O_3 and NiO which each phase has a concentration of less than 4% while XRD only appears phase peaks with a concentration more than 4%. To detect the existence of Ni, performed characterization with XRF. XRF characterization provides a concentration profile of Ni that can be seen in Figure 5.

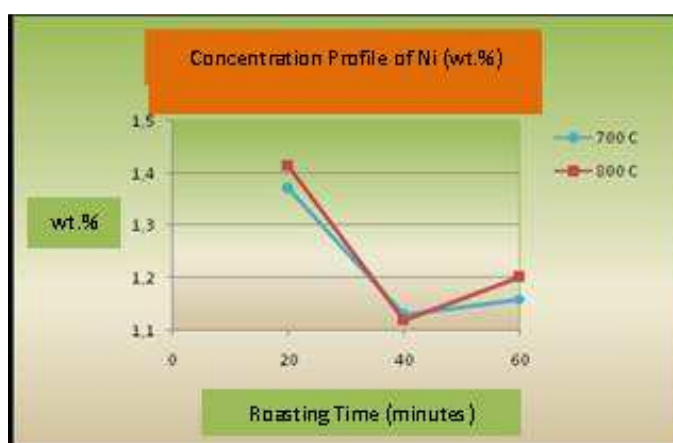


Figure 5: Concentration Profile of Ni (wt.%) on Roasting Time of Limonite

Figure 5 showed that sample roasted for 20 minutes, the increasing temperature the higher concentration of nickel up to 1.4139% from the previous concentration of 1.1903%. The increasing of nickel concentration can be seen in Table 9.

Table 9: Increasing of Nickel Concentration

Conditions	Nickel Concentration (wt.%)
Initial Samples	1.1206
After Washing and Drying Process	1.1903
After Reduction Roasting Process	1.4139

In previous research, leaching was conducted on a mixture of 25 wt.% limonite R-21 (1.01 wt.% Ni) from Indonesia and Pirotite from Ontario, Canada[7], 25 wt.% limonite (1.58 wt.% Ni), 31 wt.% limonite (1.71 wt.% Ni) from Cawse, Australia, 30-35 wt.% limonite (> 1.5 wt.% Ni) from the Falconbridge project, and 30 wt.% limonite (1.45 wt.% Ni) from the southern New Caledonia region[8, 9]. In this study, leaching was conducted on 80 wt.% limonite and 20 wt.% of coal that had been roasted at 700⁰C and 800⁰C for 40 minutes and 60 minutes. Initially, the leaching used the H₂SO₄ 0.5 M solvent, apparently, the iron and nickel were not well extracted. Then the leaching performed with a solution of HCl 1:1. This solvent HCl, as an effective solvent in the leaching, besides HNO₃ and H₂SO₄[10, 11].

In previous studies, the temperature of the leaching used between 95–105 ⁰C in a mixture of limonite and saprolite with sulfuric acid solvents[12], 85 ⁰C used in saprolite samples, and the use of room temperature continued with 60-80 ⁰C [13, 14]. In this study, the leaching was conducted at a temperature of 60 ⁰C for 15 minutes. This process parameter selection is related to the development of existing research. After the leaching process, the filtrate is characterized by AAS. The concentration of iron and nickel was determined. The wavelength, λ_{Fe} and λ_{Ni} used are 372 nm and 351.5 nm. The concentration obtained in part per million (ppm) which converted into a percentage of extraction (ext.%) using the following Equation (1). The characterization of AAS provides results as stated in Table 10.

$$ext.\% = \frac{d_f \times V_s \times C_{AAS}}{10.000 \times W_s} \quad ext.\% = \frac{d_f \times V_s \times C_{AAS}}{10.000 \times W_s} \quad (1)$$

which d_f is the dilution factor, V_s is the volume of sample (mL), C_{AAS} is the concentration of a sample (ppm), W_s is the weight of a sample (g). The best results were obtained on samples roasted at a temperature of 800⁰C for 60 minutes with an extraction percent ratio of nickel to iron as 14.42.

Table 10: Extraction Percent Ratio of Ni/Fe

No.	Sample	Ni (ext.%)	Fe (ext.%)	Extraction Percentage Ratio of Ni/Fe
1	700 ⁰ C for 40 min	29.55	50.01	0.59
2	800 ⁰ C for 40 min	8.08	42.73	0.19
3	700 ⁰ C for 60 min	7.84	41.06	0.19
4	800 ⁰ C for 60 min	44.29	3.07	14.42

CONCLUSIONS

- Limonite of Tanjung Buli Halmahera contains eight elements, i.e. Al, Si, S, Ti, V, Cr, Fe and Ni with the following concentrations:

Elements	Atomic Number	Percentage of the Weight of the Element(Wt%)
Al	13	11.0881
Si	14	3.9249
S	16	0.3787
It	22	0.8477
V	23	0.0323
Cr	24	1.9787
Fe	26	80.6290
Ni	28	1.1206

with the main phase of Gibbsite $\text{Al}(\text{OH})_3$, Goethite $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, Chromite $\text{Cr}_2\text{O}_3 \cdot \text{NiO}$, Quartz SiO_2 and Hematite Fe_2O_3 .

- The nickel concentration increases with the washing, drying and reducing roasting treatment with the following increased concentrations:

No.	Sample	Ni (ext.%)	Fe(ext.%)	Extraction Percentage Ratio of Ni/Fe
1	700 $^{\circ}\text{C}$ for 40 minutes	29.55	50.01	0.59
2	800 $^{\circ}\text{C}$ for 40 minutes	8.08	42.73	0.19
3	700 $^{\circ}\text{C}$ for 60 minutes	7.84	41.06	0.19
4	800 $^{\circ}\text{C}$ for 60 minutes	44.29	3.07	14.42

- The highest percentage of nickel extraction and the lowest percentage of iron extraction are found in samples roasted at a temperature of 800 $^{\circ}\text{C}$ for 60 minutes with an extraction percent ratio of Ni/Fe by 14.42.

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REFERENCES

1. Andika, R., W. Astuti, and F. Nurjaman. Effect of flux addition and reductant type in smelting process of Indonesian limonite ore in electric arc furnace. in *IOP Conference Series: Materials Science and Engineering*. 2019. IOP Publishing.
2. Zhang, Y., et al., Mineralogical Characteristics of the Nickel Laterite, Southeast Ophiolite Belt, Sulawesi Island, Indonesia. *Mining, Metallurgy & Exploration*, 2020. **37**(1): p. 79-91.
3. Junior, A.B.B., D.B. Dreisinger, and D.C. Espinosa, A review of nickel, copper, and cobalt recovery by chelating ion exchange resins from mining processes and mining tailings. *Mining, Metallurgy & Exploration*, 2019. **36**(1): p. 199-213.
4. Pintowantoro, S. and F. Abdul, Selective Reduction of Laterite Nickel Ore. *MATERIALS TRANSACTIONS*, 2019. **60**(11): p. 2245-2254.
5. Rout, K.R., M.V. Gil, and D. Chen, Highly selective CO removal by sorption enhanced Boudouard reaction for hydrogen production. *Catalysis Science & Technology*, 2019. **9**(15): p. 4100-4107.

6. Gaskell, D.R. and D.E. Laughlin, *Introduction to the Thermodynamics of Materials*. 2017: CRC press.
7. Ferron, C. and C. Fleming. Co-treatment of limonitic laterites and sulphur-bearing materials as an alternative to the HPAL process. in *International Laterite Nickel Symposium 2004(as held during the 2004 TMS Annual Meeting)*. 2004.
8. Nasir, Abdul, et al. "Comparative Study of Mechanically Dried Bioslurry and Commercial Fertilizers."
9. Wulandari, W., et al. Extraction of nickel from nickel limonite ore using dissolved gaseous SO₂-air. in *AIP Conference Proceedings*. 2017. AIP Publishing LLC.
10. Gupta, Bulbul, and Jaspreet Kaur. "Sources and Bioaccumulation of Toxic Organic Pollutants in the Environment: A Review on Current Scenario."
11. Kobayashi, H., et al., Selective nickel leaching from nickel and cobalt mixed sulfide using sulfuric acid. *MATERIALS TRANSACTIONS*, 2018: p. M2018080.
12. Sudibyo, S., L. Hermida, and A. Junaedi, *Application of Taguchi Optimisation of electro metal–electro winning (EMEW) for Nickel Metal from Laterite*. 2017.
13. Basturkcü, H. and N. Acarkan, Selective nickel-iron separation from atmospheric leach liquor of a lateritic nickel ore using the para-goethite method. *Physicochemical Problems of Mineral Processing*, 2017. 53.
14. Mabasha, D., G. Venkatesh, and K. Jayasimha Reddy. "Production of Synthesis Gas from Biomass and Plastic Waste using A Updraft Gasifier."
15. Kursunoglu, S. and M. Kaya, Atmospheric pressure acid leaching of Caldag lateritic nickel ore. *International Journal of Mineral Processing*, 2016. 150: p. 1-8.
16. McDonald, R. and B. Whittington, Atmospheric acid leaching of nickel laterites review: Part I. Sulphuric acid technologies. *Hydrometallurgy*, 2008. 91(1-4): p. 35-55.

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